RECOVER: REGENERATING THE STRENGTH AND VALUE OF OF THERMALLY RECYCLED GLASS FIBRES

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Abstract
Results are presented from the ReCoVeR project on the regeneration of the strength of thermally conditioned glass fibres. Thermal recycling of end-of-life glass fibre reinforced composites or composite manufacturing waste delivers fibres with virtually no residual strength or value. Composites produced from such fibres also have extremely poor mechanical performance. Data is presented showing that a short hot sodium hydroxide solution treatment of such recycled fibres can more than triple their strength and restore their ability to act as an effective reinforcement in second life composite materials. The implications of these results for real materials reuse of recycled glass fibres as replacement for pristine reinforcement fibres are discussed.

1. Introduction

The disposal of composite manufacturing waste and end-of-life composite products in an environmentally friendly manner is one of the most important challenges currently facing the industrial and academic composites community. The 2015 global production of fibre reinforced composite materials significantly exceed 10 million tons. Glass fibre was the reinforcement of choice in more than 90% of all these composites and more than 5 Mton of reinforcement grade glass fibre was used in composite production in 2015. In fact, some available data indicates that E-glass consumption could already be as high as 7 Mton when yarns are included [1,2]. This will be associated with 0.5-1 million tons of glass fibre manufacturing waste [3] most of which is landfilled. Approximately 70% of reinforcement glass fibre is used to manufacture thermoset based composites (GRP) which also produces approximately 15% manufacturing waste. Such GRP materials (both end-of-life and manufacturing waste) are difficult to recycle in an efficient manner and have historically also been disposed of in landfills. Such landfilling is rapidly becoming untenable due to legislative and landfill cost developments. The perspectives on this issue have been recently highlighted due to the accelerating growth in the use of such composite materials in transportation and wind energy sectors [4-6]. A number of processes are available for recycling such composites and thermal recycling is probably the most technologically advanced [4,5]. However, nearly all options deliver recycled glass fibres (RGF) that suffer from a lack of cost competitiveness with pristine first-pass materials.

A critical technical challenge in the development of GRP recycling technology is the 80-90% drop in the performance (and value) of RGF in comparison to its original state [5-9]. Recent studies have confirmed that the room temperature glass fibre strength can be drastically reduced by exposure to temperatures in the 300°C-600°C temperature range [7-9] typical of the many different potential GRP recycling processes. Similar behaviour has also been observed in silica and basalt reinforcement fibres [10,11]. Consequently, RGF have a very poor performance to cost ratio, and in most cases are unsuitable for reprocessing and reuse as a valuable reinforcement for composites. A breakthrough in

this field could enable such RGF to compete with pristine materials in many large volume discontinuous fibre reinforced composite applications which would have major technological, societal, economic and environmental impacts.

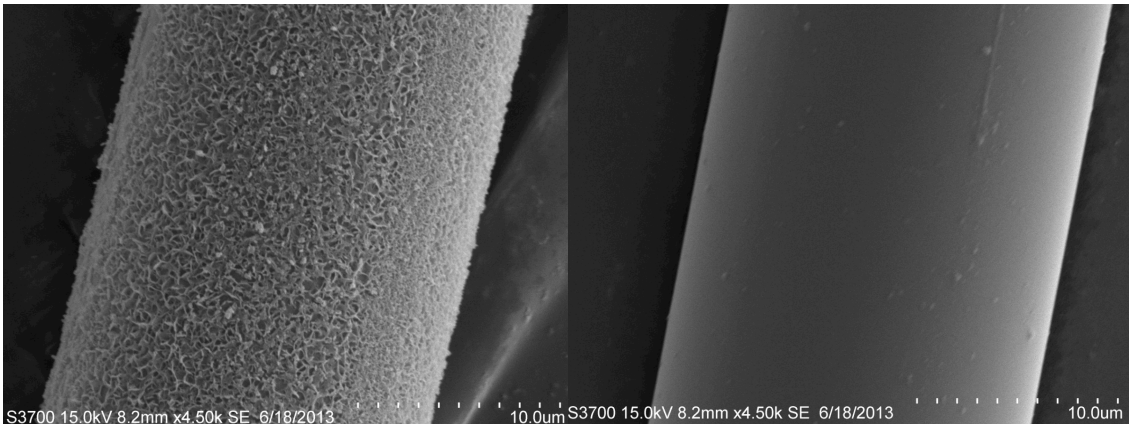
Yang et al. [12] recently demonstrated that the reinforcement potential of RGF could be significantly improved by a post treatment with hydrogen fluoride (HF) to remove the "damaged" fibre surface layer. However, given the very aggressive nature of HF and the associated safety issues, it seems unlikely that a cost-effective regeneration process could be based on HF treatment. We have been researching less aggressive chemical routes to achieve similar results. The literature generally refers to the effects of acid or alkali treatments in terms of their deleterious effects on glass fibres and the resultant lowering of composite strength. However, this body of work is almost universally predicated on maintaining the performance of strong fibres. Little if any work has been reported on the use of acid or alkali treatments to change the strength of very weak fibres. However it is well known that under the appropriate conditions a silica network can be attacked, and in some cases dissolved, by the use of sodium hydroxide (NaOH) solutions [13].

The ReCoVeR project focuses on enabling cost-effective recycling of glass fibre thermosetting composites. In particular ReCoVeR investigates the possibility of regenerating the strength of recycled glass fibres to enable their reuse as a composite reinforcement replacing the use of pristine fibre materials. In this paper we report some recent research results on the use of hot sodium hydroxide solution and subsequent silane sizing to modify the surface of thermally recycled glass fibres and the resultant effects on glass fibre and composite strength.

2. Experimental

Initial screening work on the effect of NaOH treatment on the strength of glass fibre was carried out on aminosilane coated (OC-APS) boron-free E-glass fibres supplied by Owens Corning-Vetrotex as previously described in detail [9,10,14]. A commercial chopped glass fibre product based on a boron containing E-glass formulation was supplied by PPG Fiberglass. PPG 8069 is a chopped glass fibre product designed for easy dispersion in aqueous media for the production of wet-laid non-wovens. Homopolymer polypropylene (PP) for the production of composites was purchased in the form of Goonvean DA3/60 chopped PP fibres.

The procedure for thermal conditioning of glass fibres at 500 °C for 25 minutes has been previously described in detail [9,10]. The thermally conditioned fibres were subject to different treatments. The optimisation of the conditions of these chemical treatments has been described elsewhere and is not the subject of this report [15,16]. To regenerate the fibre strength the thermally conditioned fibres were immersed in a 3M sodium hydroxide solution (NaOH) for 10 minutes at 90 °C and then neutralised by rinsing in hydrochloric acid (HCl) and then distilled water. The HCl rinse also assisted in the removal of any water glass deposits. The SEM micrograph in Figure 1a shows a typical example of these deposits on an NaOH treated heat conditioned fibre. A 1 vol% γ-aminopropyltriethoxysilane (APS) aqueous solution was used to regenerate the surface functionality of the heat treated and NaOH treated fibres. The fibres were immersed in the APS solution for 15 minutes. Samples for fibre testing were dried, however samples for GMT wet production were processed directly into the composites. Figure 1b shows the fibre surface of a heat conditioned fibre after NaOH treatment and silane treatment. This fibre exhibits the virtually featureless surface which is typically observed with new glass fibres and confirms the removal of the deposits seen in Figure 1a which can be very detrimental to the efficacy of the silane treatment [15].



(a) (b)

Figure 1. SEM of heat conditioned fibre after a) NaOH treatment, b) NaOH + HCl rinse + Silane coating.

The influence of the properties of glass fibres after thermal recycling and chemical regeneration on composite performance was further investigated by the preparation of 30% in-plane randomly oriented glass fibre reinforced polypropylene laminates (GMT) prepared by a wet-laid papermaking process and compression moulding as previously described [8]. A water jet cutter was used to cut dog bone shaped tensile test specimens out of the moulded GMT laminates according to ISO 527. A similar procedure was followed to prepare samples of unreinforced PP. The tensile tests of the composites and the unreinforced PP were performed according to the ISO 527 using an Instron 5969 universal testing machine equipped with a 50 kN load cell. The crosshead displacement was set to 1 mm/min and the strain was recorded with a video extensometer. The single fibre tensile tests were performed following the standard ASTM C1557-03. The continuous roving samples were tested at a gauge length of 20 mm, the PPG 8069 fibres were chopped to a 9 mm length and so a 5 mm gauge length was employed. For microbond testing of the samples were formed in an OV-11 vacuum oven that was purged nitrogen and heated to 220 °C. An Instron 3342 universal testing machine equipped with a 10 N load cell was used to perform the fibre tensile tests and the microbond tests as previously described [17].

3. Results and Discussion

3.1 Single fibre tensile strength of continuous rovings

The results for the average single fibre tensile test investigation are shown in Figure 2 (error ars represent the 95% confidence limits on the average value). The OC APS fibres were thermally conditioned at three different temperatures and subjected to either hot NaOH alone or hot NaOH followed by application of a simple APS sizing. The results obtained by Yang *et al* on the same fibre, thermally conditioned in an identical manner but then treated using HF etching, are also included in Figure 2 for comparison [12]. A large drop in average fibre strength (from an untreated reference value of 2.3 GPa) is observed after HT alone at all three temperatures. It was observed that after thermal conditioning the fibres were extremely brittle and difficult to handle without breakage. Hence thermal recycling not only results in a very large drop in the glass fibre performance but also makes RGF virtually impossible to process in any standard composite production equipment.

It is also worth noting that, with increasing thermal conditioning temperature, these average strength values represent a decreasing fraction of the actual fibre strength distribution of these samples. In a review of single fibre testing results in the literature Thomason has previously estimated that minimum fibre strength of approximately 0.3 GPa is required for any individual glass fibre to survive the sample preparation process [18]. Any fibres weaker than this limit which are selected from the population will not survive to contribute to the pool of strength results from any individual fibre population.

Consequently the "HT only" average values in Figure 2 must actually be considered as an upper limit on the actual average strength of these samples which may well be considerably lower due to the absence of the weakest fibre values which cannot be accessed by this test method.

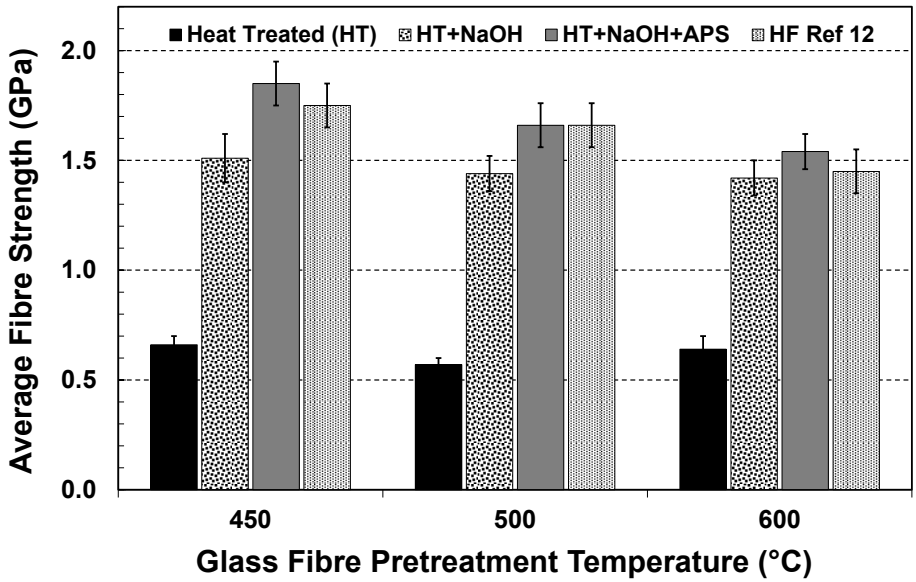


Figure 2. Influence of pretreatment temperature and ReCoVeR treatments on average fibre strength.

The results for the fibre strength recovery achieved with the hot NaOH treatment are impressive, with an strength regeneration at all three temperatures reaching approximately 1.5 GPa from the initial value of the HT fibre strength of (less than) 0.6 GPa. The addition of a simple APS sizing after the hot NaOH treatment leads to further significant (at the 95% confidence level) increases in fibre strength regeneration to well above 1.5 GPa. We consider this value of 1.5 GPa to be an important target for strength regeneration of recycled fibre in order to compete, on performance, with commercial first-pass glass fibre products. Despite the textbook value for the strength of E-glass being of the order of 3.5 GPa, Thomason and Kalinka have previously shown that the actual average strength of fibres in commercial chopped glass products can be as low as 1.8 GPa measured at a gauge length of 0.3 mm and down to 1.5 GPa measured at a 2 mm gauge length [19]. Given the well know inverse dependence of average fibre strength on test gauge length we consider that an average regenerated strength of 1.5 GPa measured at 20 mm gauge length represents a fibre strength distribution that is higher than that obtained in many commercial discontinuous glass fibre products.

The results in Figure 2 indicate a general trend for decreasing strength of the regenerated fibre strength with increasing conditioning temperature. It appears that the higher the conditioning temperature which the glass fibres have experienced then the greater the challenge of regenerating their strength. However, all treatments (even the HF data) show this tendency to some degree. This may be related to the above discussion that the average HT fibre strength values actually represent an upper limit and that the actual value is probably much lower and may well decrease with increasing conditioning temperature. Nevertheless, the data reveal that the hot NaOH based treatments deliver significant regeneration of strength in glass fibre thermally conditioned in the 450-600°C range. In particular the treatments can match the best performance of the very aggressive HF etching in terms of strength regeneration. It is most unlikely that the HF route could ever lead to a cost-effective process for regeneration the properties of recycled glass fibre. However, the data from Yang *et al* [12] clearly demonstrated the concept of glass fibre strength regeneration and also went on to show the effects on composite performance. Certainly their results using HF etching clearly showed that any such treated fibres must also be further protected and maintained by the use of fibre sizing technology similar to

standard glass fibre products [3,20]. The results shown in Figure 3 for hot NaOH treatment followed by APS sizing are always slightly higher than NaOH alone. This is likely due to the added protection of the regenerated fibre strength against the handling and sample preparation provided by the sizing.

It can be seen that significant increases of fibre strength were obtained through the hot NaOH regeneration treatments, achieving greater than a tripling of fibre strength in comparison with the thermally treated glass fibre. Consequently, the hot NaOH treatments enable regeneration of fibre strength to a level which makes reusing these fibres as a composite reinforcement a viable option.

3.2 Chopped fibres for GMT

The water-dispersible glass fibres to make GMT was a 9 mm chopped (boron containing) E-glass fibre product from PPG. The 9 mm fibre length was chosen as a compromise between processability (in particular dispersion in the sheet forming process) and the desire to be able to measure the fibre strength at a reasonable gauge length for each step in the processing. Figure 3 shows the average strengths (at 5 mm gauge length) obtained for these fibres following a combination of thermal conditioning (at 500˚C) and hot NaOH strength regeneration. The general trends observed in Figure 3 are similar to those seen in Figure 2 with the strength values in Figure 3 shifted somewhat higher due to the shorter gauge length [14,18]. These results confirm the effectiveness of the ReCoVeR treatment in regenerating the strength of thermally recycled boron-containing E-glass fibres.

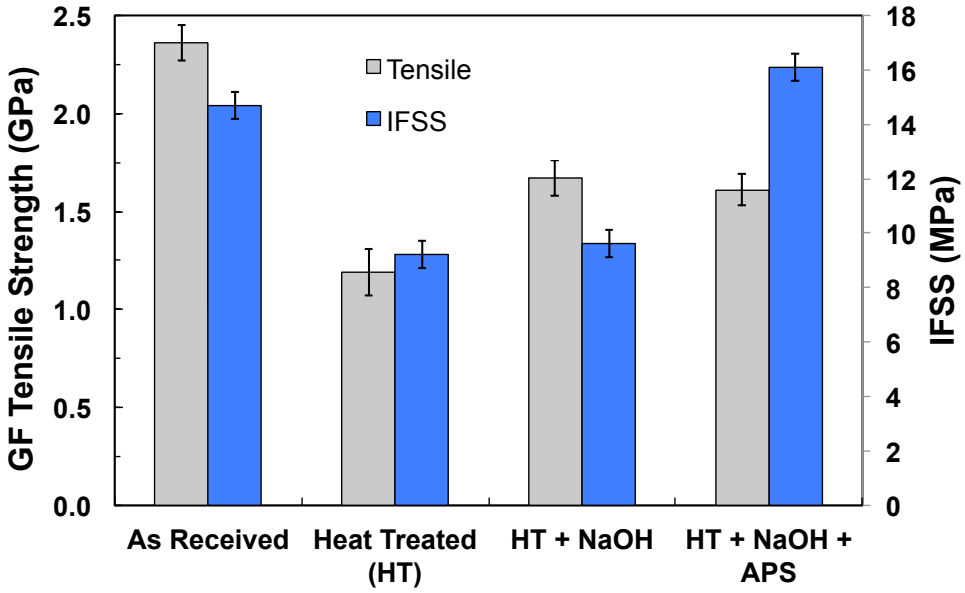


Figure 3. Influence of ReCoVeR treatments on average single fibre tensile strength of 9 mm chopped E-glass fibres and on GF-PP interfacial shear strength.

3.3 Microbond analysis of Interface Strength

We have previously observed that although the regeneration of fibre strength is a necessary condition to generate reinforcement grade RGF but is not necessarily sufficient. It is also necessary to regenerate the compatibility of the RGF with the polymer matrix of the final composite. This is generally accomplished by the application of a chemical coating (or size) to the surface of glass fibres [3,12,20]. In particular the application of a silane coupling agent has been shown to be critical to the generation of an adequate stress-transfer capability of the fibre-matrix interface [14,20]. Figure 3 also shows the results for the interfacial shear strength (IFSS) characterisation of the apparent adhesion of these RGF

fibres to the homopolymer PP used to make the GMT laminates. It can be seen that the "as received" fibres have an adequate level of IFSS with PP. It should be noted that the size on these fibres is probably optimised primarily for wet processing and only secondly for adhesion and composite performance.

The datasheet for the PPG 8069 fibres describes the product as having an aqueous silane based sizing optimised for fibre dispersion when producing a wet-laid non-woven. It is further described as compatible with a wide range of binder resin systems and also compatible with gypsum and similar systems. Consequently an IFSS level with PP of 14.7 MPa can be described as good for a product which is not developed specifically for PP. It can also be observed that the removal of the sizing by the 500˚C heat treatment significantly lowers the level of IFSS. The IFSS of 9.2 MPa seen with the HT fibres is of the same order of magnitude obtained for unsized fibres when the microbond samples are properly prepared under an inert atmosphere to avoid significant PP degradation [17]. It can further be observed that the ReCoVeR hot NaOH strength regeneration treatment alone does not regenerate the stress-transfer capability of the GF-PP interface. It is only after the APS coupling is applied to the HT+NaOH treated fibres that we see the IFSS recover. Indeed the average IFSS of the system is regenerated to an average value (16.1 MPa) which is above the "as received" fibres.

3.4 Composite performance

Figure 4 presents the results for the tensile strength of the GF-PP GMTs produced using the above range of thermally conditioned and chemically treated fibres. The strength of the GMT containing the "as received" fibres is in good agreement with the range of values reported by Thomason *et al* on GF-PP composites [21] prepared in a similar manner (also with PPG wet chopped fibres). The sample the HT fibres exhibits a large drop in tensile strength due to the low strength of the fibres and the interface in this composite. GMT tensile strength recovers by 44% when the HT fibres are given a hot NaOH treatment. Addition of silane coupling agent after the NaOH treatment results in a 74% recovery of the GMT tensile strength. It was noted that the average tensile modulus of this range of GMT's followed similar trends to the tensile strength. However, in the case of the modulus data, the differences were much smaller and in no case significant at the 95% confidence level. Further measurement of the average fibre length and orientation parameter for these laminates allowed modeling of the GMT strength using the Kelly-Tyson model. Excellent agreement was obtained when comparing the results for the GMTs in this study with the earlier published data on the strength of GMT [21,22].

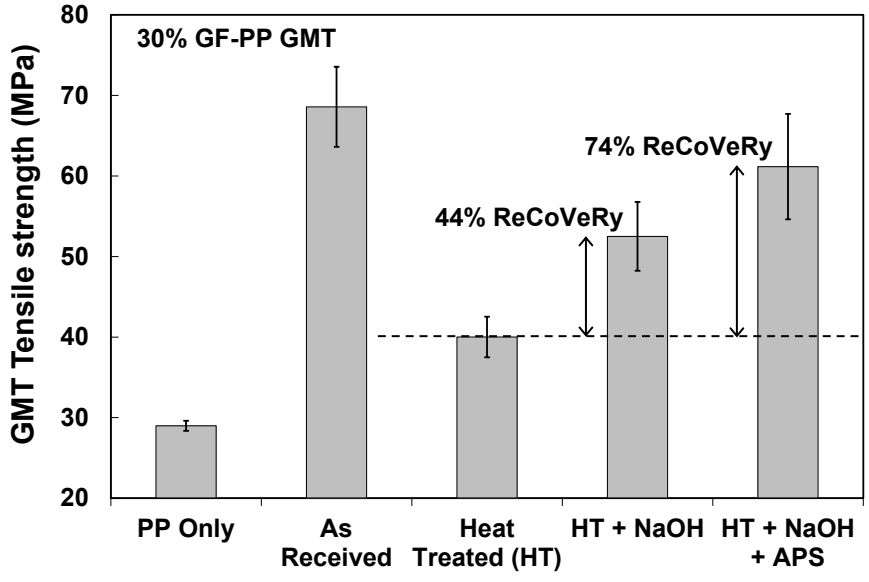


Figure 4. Influence of ReCoVeR fibre treatments on GF-PP GMT tensile strength.

3.5 Implications for real materials reuse of recycled glass fibres as replacement for pristine reinforcement fibres.

To the best of our knowledge the result shown here is one of the first published demonstrations of a chemical treatment, other than HF etching, that significantly increases the strength of thermally recycled glass fibres. Moreover, the results on GMT laminates clearly show that this regeneration of glass fibre strength can be translated directly into composite strength. Interestingly, the identification of one chemical route producing such significant fibre strength regeneration poses the question whether better chemical treatments may exist, and we are actively researching this possibility. There are many non-technical factors which will play a role in the eventual commercial profitability of any GRP recycling process. However, we believe that maximising the performance regeneration of RGF, will, enable replacement of pristine fibre products from a performance viewpoint, maximise the value of such a recycled fibre product, and increase the economic attraction of composite recycling. The development of a non-HF based glass fibre strength regeneration treatment is an exciting development in the progress towards a cost-effective GRP recycling technology.

4. Conclusions

Glass fibres lose 80% or more of their strength when exposed to temperatures typically found in GRP thermal recycling processes making them unsuitable for reuse as a composite reinforcement. The results of single fibre tensile testing presented here clearly show that up to 75% of that strength loss can be recovered by a short treatment of the fibres using hot sodium hydroxide solution. This strength recovery can be maintained and improved upon by a further application of a silane sizing. This silane layer also acts to recover the compatibility of the recycled fibre surface with a polymer composite matrix and regenerate a high level of fibre-matrix interfacial stress transfer capability. The regeneration of the recycled glass fibres performance by these simple chemical methods resulted in GF-PP GMT composites which exhibited a 74% strength recovery compared to GMT based on thermally recycled fibres which had received no further treatment. It is proposed than further optimisation of these chemical treatments can lead to further improvements in the fibre performance enabling then to be used to replace pristine first-pass fibre products used in many discontinuous glass-fibre reinforced composite applications.

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References

[1] Owens Corning Investor Presentation (slide 22) available at http://s1.q4cdn.com/942908807/files/doc_presentations/2015/Q3/Q3-Presentation-v9.pdf

[2] H. Li and J.C. Watson. Continuous Glass Fibers for Reinforcement, in Encyclopaedia of Glass Science, Technology, History and Culture (John Wiley, New York 2016)

[3] J.L. Thomason. Glass fibre sizing: A review of size formulation patents. Blurb Incorporated 2015. ISBN: 798-0-9573814-3-8. URL: http://www.blurb.co.uk/b/6244662-glass-fibre-sizing

[4] S. Job. Recycling glass fibre reinforced composites – history and progress. Reinforced Plastics 2013;57(5):19-23.

[5] S.J. Pickering. Recycling technologies for thermoset composite materials-current status. Compos Pt A 2006;37:1206-1215.

[6] G. Oliveux, L.O. Dandy, G.A. Leeke. Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties, Progress in Materials Science, 2015;72:61-99.

[7] S. Feih, E. Boiocchi, G. Mathys, A.G. Gibson, A.P. Mouritz. Mechanical properties of thermally-treated and recycled glass fibres. Compos Pt B 2011;42(3):350-358.

[8] J.L. Thomason, L. Yang, R. Meier. The properties of glass fibres after conditioning at composite recycling temperatures. Compos A 2014;61:201–8.

[9] P.G. Jenkins, L. Yang, J.J. Liggat, and J.L. Thomason. Investigation of the strength loss of glass fibre after thermal conditioning. J Mater Sci, 2015;50:1050-1057.

[10] M.R. Piggott, J.C. Yokom. The weakening of silica fibres by heat treatment. Glass technology. 1968;9:172-175.

[11] J. Militký, V. Kovačič, and J. Rubnerová. Influence of thermal treatment on tensile failure of basalt fibers. Engineering Fracture Mechanics 2002;69:1025-1033.

[12] L. Yang, E.R. Sáez, U. Nagel, and J.L. Thomason. Can thermally degraded glass fibre be regenerated for closed-loop recycling of thermosetting composites? Compos A 2015;72:167–174.

[13] R.D. Smith and P.E. Corbin. Attack of Glasses By Alkaline Solutions. J Am Ceram Soc 1949;32:195–198.

[14] L. Yang and J.L. Thomason. Effect of silane coupling agent on mechanical performance of glass fibre. J Mater Sci 2013;48:1947-1954.

[15] E. Sáez. Regenerating the strength of thermally recycled glass fibres using chemical treatments. PhD Thesis, University of Strathclyde 2016.

[16] J.L. Thomason, E. Sáez, and L. Yang. Glass Fibre Recovery. UK Patent Application July 2013.

[17] L. Yang and J.L. Thomason. Development and application of micromechanical techniques for characterising interfacial shear strength in thermoplastic composites. Polym Test 2012;31:895–903.

[18] J.L. Thomason. On the Application of Weibull Analysis to Experimentally Determined Single Fibre Strength Distributions. Compos Sci Tech 2013;77:74-80.

[19] J.L. Thomason and G. Kalinka. A technique for the measurement of reinforcement fibre tensile strength at sub-millimetre gauge lengths. Compos A 2001;32:85-90.

[20] J.L. Thomason. Glass fibre sizings: A review of the scientific literature. Blurb Incorporated 2012. ISBN: 798-0-9573814-1-4. URL: http://www.blurb.co.uk/b/6244677-glass-fibre-sizings

[21] J.L. Thomason, M.A. Vlug, G. Schipper, and H.G.L.T. Krikor. The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: Part 3 Strength and strain at failure. Composites 1996;27:1075-1084.

[22] J.L. Thomason, U. Nagel, L. Yang, and E.R. Sáez. Regenerating the strength of thermally recycled glass fibres using hot sodium hydroxide. Compos Part A 2016 submitted.